Bond Strength of Chlorine Peroxide

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The bond strength of chlorine peroxide (ClOOCl) is studied by photoionization mass spectrometry. The experimental results are obtained from the fragmentation threshold yielding ClO^+, which is observed at 11.52 ± 0.025 eV. The O−O bond strength $D°$ is derived from this value in comparison to the first ionization energy of ClO, yielding $D°_{298} = 72.39 \pm 2.8$ kJ mol^{-1}. The present work provides a new and independent method to examine the equilibrium constant K_{eq} for chlorine peroxide formation via dimerization of ClO in the stratosphere. This yields an approximation for the equilibrium constant in the stratospheric temperature regime between 190 and 230 K of the form $K_{eq} = 1.92 \times 10^{-27}$ cm^3 molecules^{-1} × exp(8430 K/T). This value of K_{eq} is lower than current reference data and agrees well with high altitude aircraft measurements within their scattering range. Considering the error limits of the present experimental results and the resulting equilibrium constant, there is agreement with previous works, but the upper limit of current reference values appears to be too high. This result is discussed along with possible atmospheric implications.

Introduction

ClOOCl is efficiently formed in the stratosphere from ClO, if the temperature is low enough to permit dimerization. Three isomers of Cl_2O_2 are known (ClOOCl, $ClClO_2$, and ClOClO), of which ClOOCl is the most stable one.[1,2] Therefore, dimerization of ClO yields preferably chlorine peroxide ClOOCl, whereas the other isomers are formed with considerably lower efficiency.[3,4] ClOOCl is a key compound for the understanding of strong stratospheric ozone loss in the cold stratosphere, which is regularly observed in polar spring.[5,6] The isomer chlorine peroxide ClOOCl is the key species in the major ozone loss cycle under polar stratospheric conditions:[5−7]

$$2ClO + M \rightleftharpoons ClOOCl + M \quad (1)$$

$$ClOOCl + h\nu \rightarrow ClOO + Cl \quad (2)$$

$$ClOO + M \rightarrow Cl + O_2 + M \quad (3)$$

$$2(Cl + O_3 \rightarrow ClO + O_2) \quad (4)$$

$$\text{net:} \quad 2O_3 + h\nu \rightarrow 3O_2 \quad (5)$$

Reactions 2 and 3 proceed probably in a concerted manner, where the intermediate ClOO is produced with sufficient energy so that it likely dissociates spontaneously under stratospheric conditions.[8]

The ground-state geometry of ClOOCl has been reported by Birk et al.,[9] which has been recently questioned based on coupled cluster calculations.[10] In particular, the O−O bond length is found to be shorter than in previous experimental work.

The bond strength of ClOOCl at 298 K has been reported before. The values range between 69 ± 3 kJ and 81.6 ± 2.9 kJ mol^{-1}.[11,12] Cox and Hayman report 72.5 ± 3 kJ mol^{-1}.[13] This bond strength as well as the equilibrium constant for ClOOCl-formation according to eq 1 are crucial quantities with respect to the importance of the ozone loss mechanism shown in eqs 1−5. Small changes in ClO−OCl bond strength may significantly change the equilibrium of eq 1 in the stratosphere. Moreover, discrepancies between measurements of chlorine oxides in the stratosphere and model predictions are reported which may possibly be connected with uncertainties in stratospheric chlorine chemistry.[14,15] Recent field measurements by von Hobe et al.[16] and Stimpfle et al.[17] indicate that there are indeed discrepancies in the equilibrium constant for ClOOCl-formation.

The motivation for the present work is the importance of ClO chemistry in the polar stratosphere including existing uncertainties that are related to the dimerization of ClO. We report the ClO−OCl bond strength using photoionization mass spectrometry as an alternative laboratory approach compared to previous

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works, where the dimerization equilibrium of ClO was investigated.[11−13]

Experimental Section

The experimental setup consists of the following components: (i) a flow tube for ClO and ClOOCl production; (ii) a tunable vacuum−ultraviolet (VUV) radiation source (laser-produced plasma, pulse length = 25 ns, $\sim 10^9$ photons/s at a bandwidth of 0.8 nm) between 8 eV $\leq E \leq$ 25 eV photon energy; (iii) a time-of-flight mass spectrometer (TOF) for cation separation and detection.[4] ClO is generated in the flow tube by the reaction: $Cl + OClO \rightarrow 2\ ClO$, using a gas mixture of 5% Cl_2 in He for Cl production in a microwave discharge at typically p = 5 hPa. The OClO source has been described before.[18] Chlorine peroxide is efficiently produced by cooling the flow tube to 170 K, as reported in previous work.[4] We derive from our prior photolysis work the contribution of $ClClO_2$ to Cl_2O_2 to be 17 ± 2%, whereas the remaining 83 ± 2% contribution is due to ClOOCl.[4] It is assumed that the contribution of $ClClO_2$ is essentially due to residual humidity in the cold flow system, which promotes the formation of this species via heterogeneous reactions. The formation of Cl_2O_3 is avoided by titrating the OClO with atomic chlorine. Thus, no mass signals from $Cl_2O_3^+$ (m/z = 118, 120, 122) are observed in photoionization mass spectra. Further, no evidence from mass signals pointing to the formation of higher chlorine oxides in the flow tube is found (cf. ref 19). The gaseous sample emerges from the flow tube into a high vacuum recipient. It is ionized in the ionization region of the TOF by tunable VUV-radiation at $p \leq 10^{-3}$ Pa, i.e., under collision-free conditions. The ionization and fragmentation thresholds of selected mass channels are obtained by scanning the photon energy while measuring the cation intensity. The intensity of the ionizing VUV-radiation is measured simultaneously, so that photoionization mass spectra as well as photoion yields are reliably normalized to the VUV photon flux. The absolute photon energy scale is established by using the autoionization of molecular oxygen as well as rare gases.[20]

Results and Discussion

Bond Strength of ClO—OCl. Photoionization mass spectrometry is used to determine the O−O bond strength of ClO−OCl. This is accomplished by measuring the ionization energy of ClO and the fragmentation threshold of ClO^+ formation from ClOOCl. The energy difference between both quantities yields the ClO−OCl bond strength.

The ionization energy of ClO (IE(ClO)) is obtained from the ClO^+ photoion yield of the room-temperature ClO sample, where no chlorine peroxide is present in the flow tube:

$$ClO + h\nu \rightarrow ClO^+ + e^- \tag{6}$$

as shown in Figure 1a. This yields IE(ClO) = 10.85 ± 0.013 eV. The error limit of the threshold energy is determined from the experimental uncertainty, where the ion intensity rises above the noise level, as follows from Figure 1a. Each data point corresponds to the sum of repeated scans of the ClO^+ yield as a function of photon energy. This measurement confirms our earlier work, but the error limit is significantly reduced.[21] Note that Thorn et al. have reported a somewhat higher ionization threshold value of 10.885 ± 0.016 eV.[22] This discrepancy is essentially the result of a different way of determining the ionization threshold. We use throughout this work the approach outlined by Traeger and McLoughlin,[23] where the threshold energy is found by linear extrapolation of the ion intensity right above the onset to the pre-threshold level, similar to previous work.[24] This aspect is of central importance to the present work, where differences in threshold energies are used to determine the ClO−OCl bond strength. These must be determined exactly in the same way in order to avoid artifacts that may come from different ways to determine ionization or fragmentation thresholds.

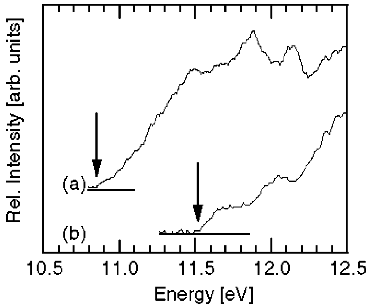

Figure 1. Photoion yield of ClO^+ recorded at different experimental conditions: (a) T = 298 K; (b) T = 170 K. The arrows indicate the threshold energies. The horizontal lines mark the zero level of cation intensity.

The appearance energy of ClO^+ from ClOOCl is measured by cooling the flow tube to T = 170 K. This yields an increased threshold energy relative to that of neat ClO, corresponding to 11.52 ± 0.025 eV (see Figure 1b). This threshold is determined in the same way as the ionization energy of ClO, indicating that ClO is efficiently bound in Cl_2O_2, where predominantly ClOOCl is formed.[4] Although, ClOOCl represents 83% of the Cl_2O_2 sample, as outlined in the previous section, it is important to find evidence whether exclusively this majority species contributes to the experimental threshold energy. The photoion yield of ClO^+ is characterized by two distinct steps above the onset energy. These steps occur at the threshold (E = 11.52 eV) and near 11.84 eV, respectively. The energy difference of ≈0.32 eV is too large to be due to any vibrational fine structure of the neutral (cf. ref 25) or the cation. It is rather assumed that either close lying direct ionization processes from outer occupied orbitals,[26] or autoionization features contribute to the structured photoion yield of ClO^+ in the threshold regime.

The origin of ClO^+ that contributes to this threshold value is discussed in the following with respect to other channels that may possibly be active at the threshold energy: First, ClOOCl is formed efficiently upon dimerization of ClO, corresponding to chlorine peroxide formation, at low temperature.[4] In this case, the appearance energy of ClO^+ is due to fragmentation from $ClOOCl^+$, so that this value can be used to determine the bond strength of ClO−OCl. However, other Cl_xO_y minority species may also contribute to the ClO^+ threshold. The appearance energy of the process $ClClO_2 + h\nu \rightarrow ClO^+ + Cl + O + e^-$ is calculated to be 14.28 eV (cf. data from ref 27). Even if instead of the neutrals Cl + O the molecular fragment ClO is formed upon dissociative photoionization, one derives a threshold value of 11.49 eV, which is slightly below the value of 11.52 ± 0.025 eV, that is deduced from Figure 1b. Thus, the threshold energies of these processes starting from ClOOCl and $ClClO_2$ are quite similar to each other, so that they will be difficult to distinguish, if they occur with the same intensity. Evidently, this is not the case for the following reasons: (i) $ClClO_2$ is only a minority species in the sample; (ii) both isomers should have the same fragmentation cross section in the threshold regime; (iii) the fragmentation threshold starting from $ClClO_2$ would imply that the cation undergoes massive rearrangement processes after vertical excitation, which appears to be unlikely at the threshold energy. In contrast, the process starting from ClOOCl corresponds to a rupture of the ClO−OCl$^+$ bond. Contributions to the ClO$^+$ yield from higher chlorine oxides are ruled out, as pointed out in the previous section. Furthermore, contributions to the ClO$^+$ threshold from the reactant OClO are ruled out, since the fragmentation threshold is found at 13.40 ± 0.04 eV.[28] Therefore, one expects for the majority species ClOOCl a clearly visible threshold that leads to ClO$^+$ formation at 11.52 eV (cf. Figure 1b), which is assigned to dissociative photoionization of ClOOCl:

$$\mathrm{ClOOCl} + h\nu \rightarrow \mathrm{ClO}^+ + \mathrm{ClO} + \mathrm{e}^- \tag{7}$$

The difference in threshold energies between processes 7 and 6 gives directly the bond dissociation energy of ClOOCl, using the stationary electron convention and by considering thermal effects.[23] First, we correct the experimental results to $T = 0$ K, using the experimental value from Figure 1a: IE(ClO) = 10.85 ± 0.013 eV. The heat of formation of ClO is well-known: $\Delta_f H°_0$ (ClO) = 101.03 ± 0.1 kJ mol^{-1}.[29] This yields together with IE(ClO): $\Delta_f H°_0$ (ClO$^+$) = 1147.9 ± 1.3 kJ mol^{-1}. This value is somewhat smaller than that reported by Thorn et al.,[22] since they used a larger value for the first ionization energy of ClO, as mentioned above. The appearance energy yielding ClO$^+$ from ClOOCl (AE(ClO$^+$/ClOOCl)) (see Figure 1b) has been recorded at $T = 170$ K. This value is corrected to $T = 0$ K according to[22,23]

$$\mathrm{AE}_0\,(\mathrm{ClO}^+/\mathrm{ClOOCl}) = \mathrm{AE}_{170}\,(\mathrm{ClO}^+/\mathrm{ClOOCl}) + [H_{170} - H_0] - 2.5RT \tag{8}$$

The thermal correction is obtained from the heat capacity estimates of ClOOCl similar to calculations by Abramowitz and Chase,[29] and the most recent JANAF compilation.[30] Instead of the data from these references we use slightly different, rounded vibrational frequencies, which are based on more recent experimental work by Jacobs et al.[25] including vibrations communicated in earlier work: $\nu_1 = 754$ cm^{-1}, $\nu_2 = 543$ cm^{-1}, $\nu_3 = 320$ cm^{-1}, $\nu_4 = 127$ cm^{-1}, $\nu_5 = 648$ cm^{-1}, and $\nu_6 = 419$ cm^{-1}. These values consider the dominant abundance of the ^{35}Cl isotopomer and appear to be more reliable than earlier estimates (cf. ref 29). We note that the difference in thermal correction between both approaches is of the order of 0.055 kJ mol^{-1} for the correction from 170 to 0 K. However, this difference increases more significantly to 0.2 kJ mol^{-1} for the thermal correction from 0 to 298 K (see below).

The present thermal correction yields AE$_0$ (ClO$^+$/ClOOCl) = 11.555 ± 0.025 eV. Ionic fragmentation of ClOOCl yields ClO$^+$ + ClO (cf. eq 7). The sum of the heats of formation of these products is: $\Delta_f H°_0$ (ClO$^+$) + $\Delta_f H°_0$ (ClO) = 1248.93 ± 1.36 kJ mol^{-1}. One obtains from this value by subtracting AE$_0$ (ClO$^+$/ClOOCl) the heat of formation of ClOOCl: $\Delta_f H°_0$ (ClOOCl) = 134.07 ± 2.8 kJ mol^{-1}. This value compares well to previous experimental work,[12,13] and theoretical studies that range from 123.1 to 143.2 kJ mol^{-1}.[27,31−33]

The bond strength of chlorine peroxide at $T = 0$ K is obtained from

$$D°_0\,(\mathrm{ClO{-}OCl}) = 2\,\Delta_f H°_0\,(\mathrm{ClO}) - \Delta_f H°_0\,(\mathrm{ClOOCl}) \tag{9}$$

yielding $D°_0$ (ClO−OCl) = 67.99 ± 2.8 kJ mol^{-1}. Note that this value is similar to results from earlier theoretical work, where 79.16 kJ mol^{-1} are derived with a considerable error limit of ±12.5−20.9 kJ mol^{-1}.[5] $D°_0$ (ClO−OCl) is corrected to $T = 298$ K so that it can be compared to previous works.[11−13] This is accomplished by using $\Delta_f H°_{298}$ (ClO) = 101.63 ± 0.1 kJ mol^{-1}.[29,30] $\Delta_f H°_{298}$ (ClOOCl) is obtained from $\Delta_f H°_0$ (ClOOCl) along with thermal corrections as outlined above.[23,25,29,30] We derive from this $\Delta_f H°_{298}$ (ClOOCl) = 130.87 ± 2.8 kJ mol-^{1}. Finally, we obtain according to eq 9 for $T = 298$ K: $D°_{298}$ (ClO−OCl) = 72.39 ± 2.8 kJ mol-^{1}. This value compares well with previous works (see Table 1). Small, but significant discrepancies compared to the current JPL-evaluation[34] will be discussed in greater detail in the following section.

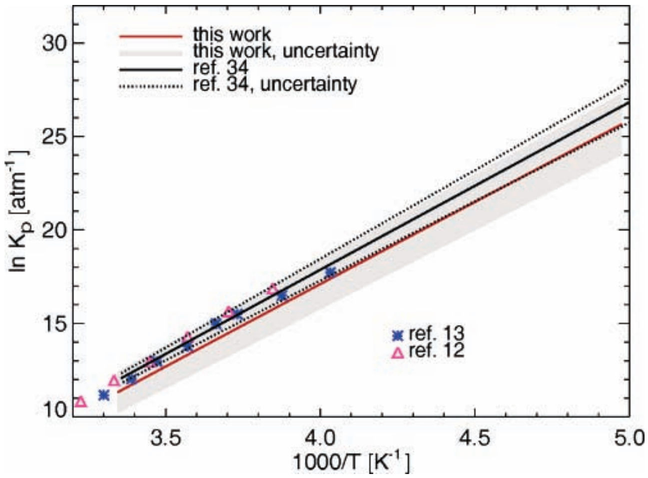

Figure 2. Temperature dependence of the equilibrium constant K_p of reaction 1 as a function of the reciprocal temperature. Experimental results from laboratory work,[12,13] the recommended values from ref 34, and results from this work are included.

TABLE 1: Comparison of the ClO−OCl Bond Strength at $T = 298$ K: $D°_{298}$ (ClO−OCl) Derived from Experimental Work

reference	$D°_{298}$ (ClO−OCl), kJ mol^{-1}
Basco and Hunt[11]	69 ± 3
Nickolaisen et al.[12]	81.6 ± 2.9
Cox and Hayman[13]	72.5 ± 3
this work	72.39 ± 2.8

Atmospheric Implications. From the experimental bond dissociation energy of chlorine peroxide derived from the present work, we can calculate the equilibrium constant K_{eq} for reaction 1, which is expressed in terms of the reaction entropy $\Delta_r S$ and enthalpy $\Delta_r H$:

$$K_{eq} = \frac{RT}{N_A}\, e^{\Delta_r S/R}\, e^{-\Delta_r H/RT} \tag{10}$$

where N_A is the Avogadro constant and R is the universal gas constant. The temperature dependence of $\Delta_r S$ and $\Delta_r H$ is considered in order to obtain accurate results over a wide temperature range. $\Delta_r S(T)$ is derived from third law entropies of ClO and ClOOCl, as described by Chase,[30] using the vibrational frequencies derived by Jacobs et al. (cf. previous section).[25] $\Delta_r H(T)$ is equivalent to the bond dissociation energy of ClOOCl calculated from $\Delta_f H°$(ClO) and $\Delta_f H°$(ClOOCl) (see eq 9) using the thermal correction to account for its temperature dependence.[29,30]

Figure 2 shows a van't Hoff plot of the equilibrium constant K_p as a function of T^{-1}. K_p [atm^{-1}] is derived from K_{eq} [cm^3/molecule] using eq 10, where $K_p = K_{eq}(T)/(RT)$. Thus, the present results can be directly compared to earlier works, which are also included in Figure 2.[12,13,34] The error limits of K_p are directly determined by the error limit of the ClO−OCl bond strength given above. This is due to the fact that the uncertainty of $\Delta_r S$ is negligible compared to the uncertainty of $\Delta_r H$ (cf. ref 30). The present value of K_{eq} is lower over the entire temperature

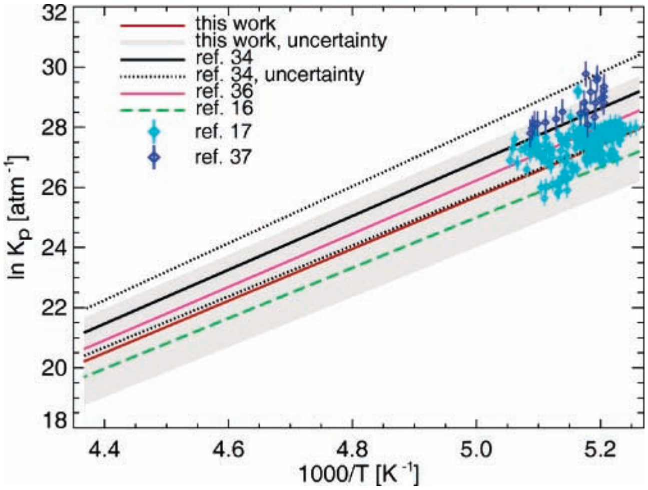

Figure 3. Temperature dependence of the equilibrium constant K_p of reaction 1 as a function of the reciprocal temperature in the regime of stratospheric temperatures. Experimental results from field measurements,[16,17,36] the recommended values from ref 34, and results from this work are included. The measurements from refs 17 and 37 were conducted in the Arctic winter 1999/2000. They are shown for $p <$ 100 hPa (see diamonds with error bars).

range shown in Figure 2 (200 K $< T <$ 300 K) than K_{eq} given by the current JPL evaluation[34] and previous laboratory measurements.[12] Good agreement is found with results reported by Cox and Hayman.[13] K_{eq} from the present work practically coincides with the lower limit of the current JPL recommendation.[34] These discrepancies lie within the uncertainty range of the present results. This suggests that there is general agreement between the different K_{eq} values. However, the present results allow us to exclude the upper uncertainty limit of the JPL recommendation for K_{eq}.[34] Furthermore, the difference between the JPL recommendation for K_{eq} and the values reported here has significant implications for the equilibrium partitioning of ClO and ClOOCl in the stratosphere, where simulated mixing ratios of ClO for night time conditions are extremely sensitive to the exact value of the bond strength of chlorine peroxide.[16] Specifically, for a given amount of active chlorine (see below) at $T = 190$ K, the equilibrium ClO concentrations calculated from the two different K_{eq} values, i.e., from ref 34 and this work, differ by up to a factor of 2.

The overall temperature dependence of K_{eq} is obtained by fitting the results derived from eq 10 over the temperature range between 150 and 400 K (see Figure 2). This can be expressed as

$$K_{eq} = 1.61 \times 10^{-27}\left(\frac{T}{300}\right)^{-0.29} e^{8480/T} \tag{11}$$

However, in stratospheric chemistry models usually a parametrization of the form $K_{eq} = A \times \exp(B/T)$ is used.[34] We approximate the results from eq 10 and 11 in the typical temperature range of the polar stratosphere between 190 and 230 K using $A = 1.92 \times 10^{-27}$ cm^3 molecule^{-1} and $B = 8430$ K. This is compared in Figure 3 to the recommended JPL value[34] and various estimates based on night-time field measurements, employing the chemical-conversion resonance-fluorescence technique,[35] where results from refs 16, 17, 36, 37 are included.

At night time, when photolysis effects are negligible and the probed air parcels can be assumed to be in a thermal equilibrium. K_{eq} is deduced from observed ClO and ClOOCl stratospheric concentrations, using

$$K_{eq} = \frac{[\mathrm{ClOOCl}]_{night}}{[\mathrm{ClO}]_{night}^{\,2}} \tag{12}$$

The analysis of in situ ClO high altitude aircraft measurements by Avallone and Toohey and estimated ClOOCl mixing ratios, assuming full chlorine activation, yield a somewhat higher equilibrium constant than derived from the present work.[36] This value of K_{eq} is still significantly lower than the value reported in ref 34. Results based on in situ ClO and ClOOCl measurements for solar zenith angles SZA > 95°, conducted in the Arctic stratosphere on board the high altitude aircraft ER-2 in winter 1999/2000 by Stimpfle et al.,[17] agree with the results of the present work. Von Hobe et al. found an even lower value for K_{eq} based on in situ ClO and ClOOCl aircraft measurements conducted in the Arctic winter 2002/2003.[16] These aircraft measurements[16,17,36] generally confirm the equilibrium constant of the present work within their scatter range and provide strong evidence that the current recommendation[34] slightly overestimates K_{eq}. On the other hand, another evaluation,[37] that is based on ClO measurements which were obtained from a balloon-borne instrument, launched on March 1, 2000, before sunrise from Esrange (67.5° N, 21.0° E) near Kiruna, North Sweden, supports slightly higher values for K_{eq} than the recommended value. Specifically, night-time ClO mixing ratios measured during the ascent between 96 and 99° SZA are used in the previous analysis.[37] The corresponding ClOOCl mixing ratios were estimated from ClO daylight measurements based on the assumption that the total amount of reactive chlorine ClO_x is given by

$$\mathrm{ClO}_x = \mathrm{ClO} + 2\mathrm{ClOOCl} \tag{13}$$

and that during daylight (SZA < 88°) the air parcels are in a photochemical steady state with the ClOOCl photolysis (eq 2) which is progressing much faster than the thermal decay (eq 1). Then one obtains

$$[\mathrm{ClOOCl}]_{day} \approx \frac{k_f\,[\mathrm{ClO}]_{day}^{\,2}\,M}{J} \tag{14}$$

Here, k_f is the rate constant for the ClOOCl formation, which is taken from ref 34 (see eq 1), J is the photolysis rate constant (see eq 2) derived from absorption cross sections recommended by Burkholder et al.,[38] and M is the air density. For pairs of $[\mathrm{ClO}]_{day}$ and $[\mathrm{ClO}]_{night}$ taken on the same levels of potential temperature Θ, where $\Theta = T(1000/p)^{R/c_p}$, with the atmospheric pressure p measured in hPa and the molar heat capacity of air c_p,[39] conservative ClO_x concentrations $[\mathrm{ClO}_x]$ can be estimated over time scales for which the impact of heating or cooling can be neglected. This corresponds to adiabatic conditions, where in the atmosphere air parcels remain on a level of constant potential temperature. Thus, using eqs 12−14 gives

$$K_{eq} = \frac{[\mathrm{ClO}_x] - [\mathrm{ClO}]_{night}}{2\,[\mathrm{ClO}]_{night}^{\,2}} \tag{15}$$

with an uncertainty of 40−45% for K_{eq} calculated by error propagation. ClO mixing ratios were averaged in Θ intervals of ±5 K in the range 380 K $\leq \Theta \leq$ 485 K. This is equivalent to 40 hPa $\leq p \leq$ 98 hPa. We note that calculations of backward trajectories show that the origin of the air masses sampled in the balloon ascent and descent are located sufficiently close together so that it is ruled out that different air masses were probed.[37] Reasons for the discrepancy between balloon observations[37] and aircraft observations,[16,17,36] in particular those carried out in the same winter,[17] are currently unknown. However, it appears to be possible that the high altitude aircraft measurements,[17] that were taken in early winter 1999/2000 (between 000114 and 000203), do not reflect the same amount of chlorine activation than the balloon measurements that were conducted in the beginning of March 2000.[37] Specifically, model simulations indicate that at the end of February 2000 chorine reactivation occurred.[37] Possibly, discrepancies in K_{eq} values could be rationalized by these different atmospheric conditions. Finally, it is noted that, except for some values at low temperatures derived from the measurements in the Arctic winter 1999/2000,[17,37] all results reported from field measurements[16,17,36,37] lie within the uncertainty range of K_{eq} from the present work.

Conclusions

The thermal stability of ClOOCl is studied by photoionization mass spectrometry. The ClO−OCl bond dissociation energy is determined, yielding $D°_{298} = 72.39 \pm 2.8$ kJ/mol. The ClO−OCl bond dissociation energy corresponds to an equilibrium constant $K_{eq} = 1.61 \times 10^{-27} \times (T/300)^{-0.29} \times \exp(8480/T)$, which is in agreement with previous laboratory experiments[12,13] and field measurements[16,17,36] within the given uncertainties. Nonetheless, differences in K_{eq} within this uncertainty range have already significant implications on the equilibrium partitioning of ClO and ClOOCl in the cold dark stratosphere. K_{eq} reported in this work is in accordance with results from high altitude aircraft measurements,[16,17,36] and somewhat lower than the value recommended by the current JPL evaluation.[34] This allows us to exclude the upper uncertainty limit given in ref 34. The present findings imply that ClOOCl is slightly less stable than previously thought, and consequently, there should be higher ClO mixing ratios in the cold stratosphere for nighttime conditions than follows from the currently recommended value of K_{eq}. A lower value of K_{eq} is expected to shift the partitioning between the ClO dimer and the ClO−BrO cycle toward the latter one, but the overall ozone loss rate in the Arctic winter stratosphere is only marginally affected by this slight change.[16,17] Reasons for the discrepancies between several field measurements[16,17,36] and the present results based on laboratory experiments cannot be fully resolved, warranting further laboratory studies and field measurements. Nonetheless, the present work utilizes a novel approach to determine the ClO−OCl bond strength, which serves to derive K_{eq} from laboratory measurements.

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